

SELECTIVE FLUORINATION OF COALS: STRUCTURE AT REACTIVE SITES BY HIGH RESOLUTION TRIPLE RESONANCE SOLID STATE NMR

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INTRODUCTION

As part of our program to define the chemical reactivity of coals, we are systematically investigating methods to introduce fluorine into specific sites in the organic matrix of these materials. The methodology is guided by analysis methods appropriate for solid derivatives. The spectroscopic technique that we use most heavily is solid state NMR.¹ In addition to the triple resonance experiments of reference (1), we have recently achieved the capability to observe ^{19}F directly. The utilization of the large ^{19}F chemical shift dispersion and cross correlation with the ^{13}C chemical shift will provide a powerful approach for analysis in these complex materials. We use Fourier transform infrared spectroscopy (FTIR) as a rapid method to assess fluorine incorporation into the coal matrix.

RESULTS AND DISCUSSION

Treatment of North Dakota lignite (Argonne Premium Coal No.8) with Sulfur Tetrafluoride. The chemistry of sulfur tetrafluoride with organic carbonyl compounds is well known.^{2,3} Under mild reaction conditions it converts carboxylic acid functionality into acyl fluoride moieties. The reaction proceeds with aliphatic and aromatic acids although the latter require acid catalysis in some cases. The following experimental reports our initial trials using SF_4 to convert carboxylic acid functional groups in coal into acyl fluoride residues. Dry lignite (110°C vacuum oven, 24 h), 0.5 g, is placed in a monel pressure vessel and evacuated. Sulfur tetrafluoride, 15 g, is transferred to this vessel, cooled in a dry ice/acetone bath. The reaction is accomplished by warming the vessel to the desired temperature and allowing the mixture to stand for the prescribed time. Excess SF_4 and gaseous byproducts of the reaction are destroyed in aqueous KOH traps. The coal is then washed with water until the filtrate is neutral and then dried at 110°C.

The reactivity of the coal with SF_4 is dependent on pretreatment. Lignite, as received, produces a material that shows minor reaction after contact with SF_4 for 72 h at 110°C. Reaction progress is judged by the relative intensity of the acid fluoride absorption in the infrared spectrum (IR) at 1830 cm^{-1} and by the ^1H - ^{19}F - ^{13}C double cross polarization (DCP)/MAS ^{13}C NMR spectrum. Washing the coal with 1N HCl or with citric acid⁴ and then with water until the filtrate is neutral to pH paper, followed by overnight drying, yields a much more reactive coal. The source of the difference in reactivity is suggested in the FTIR spectra of the APC #8 lignite and of the HCl washed material, shown in Figure 1a and b, respectively. The change in the carbonyl absorption indicates the

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Table 1

Crystalline Phases in Fe-S System

Formula	Crystal Structure	Lattice Parameters Å		
Fe ₇ S ₈	HCP	a = 6.867	c = 17.062	
FeS	HCP	a = 5.967	c = 11.735	
Fe ₃ S ₄	HCP	a = 3.47	c = 34.5	
Fe _{1-x} S	HCP	a = 6.88	c = 22.90	
FeS ₂	Cubic	a = 5.417		
FeS	Cubic	a = 5.423		
Fe ₇ S ₈	Monoclinic	a = 11.902	b = 6.859	c = 22.787
β-Fe _{1-x} S	HCP	a = 6.894	c = 40.15	
Fe ₉ S ₈	Tetragonal	a = 3.679	c = 5.047	
FeS ₂	Orthorhombic	a = 4.436	b = 5.414	c = 3.381
Fe ₃ S ₄	Cubic	a = 9.876		
FeS	Tetragonal	a = 3.676	c = 5.032	

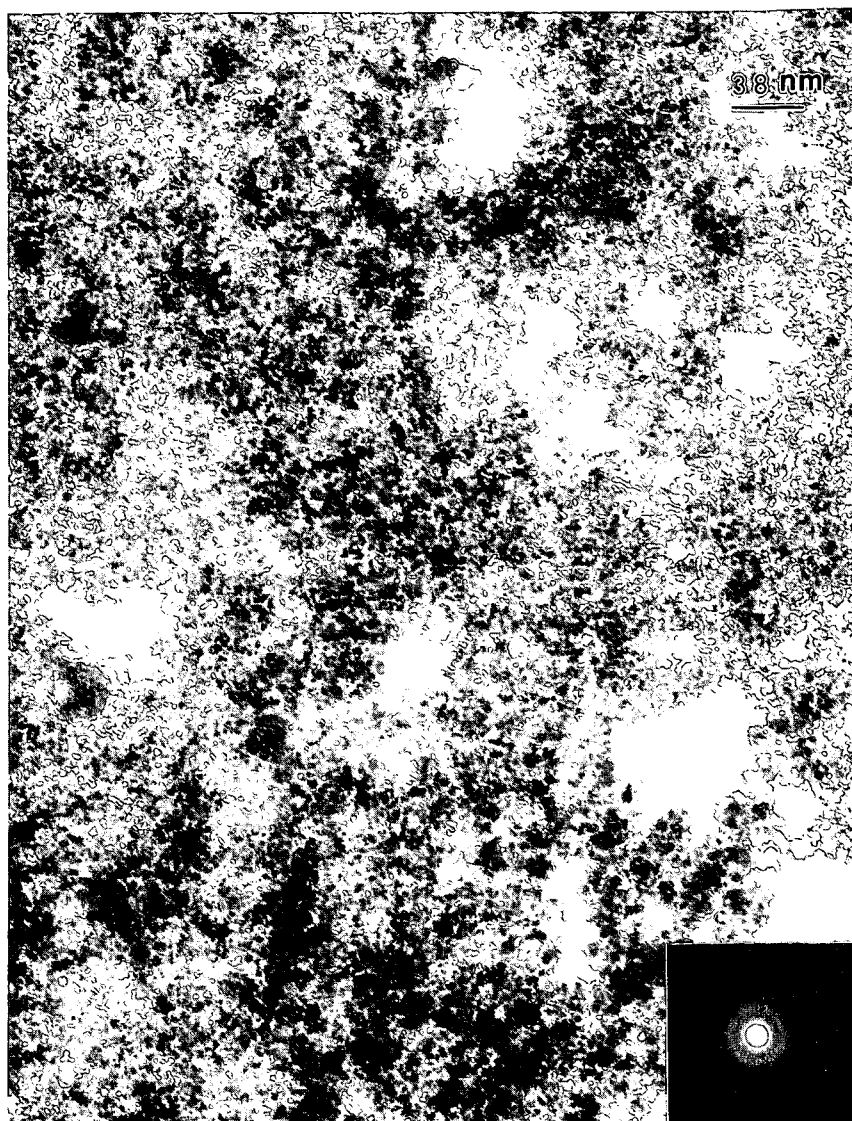


Figure 1. Transmission electron micrograph from the as-received Fe_2O_3 catalyst (inset). Microdiffraction pattern showing diffuse rings.

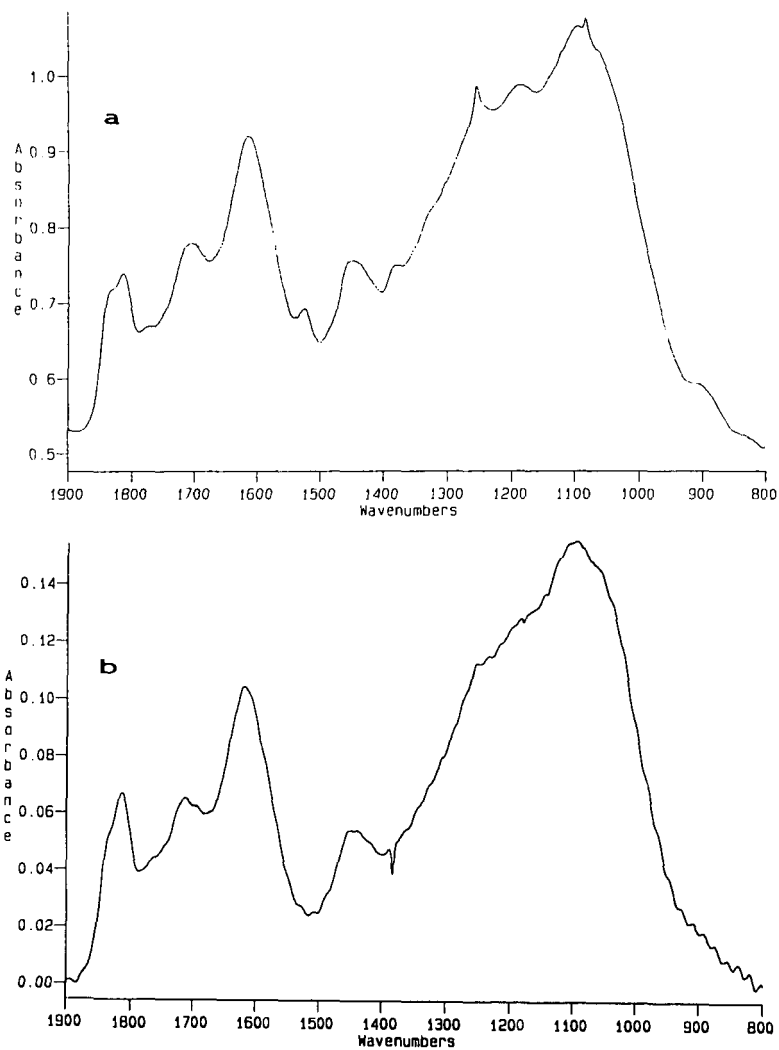


Figure 2. Infrared spectra (KBr pellet) of the products obtained from fluorination of North Dakota lignite with SF_6 , (a) at 110°C for 15 h, (b) at 170°C for 18 h.